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THE SEPARATION AND IDENTIFICATION OF  
ACIDS IN LOW TEMPERATURE TAR

BY

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THESIS

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I HEREBY RECOMMEND THAT THE THESIS PREPARED UNDER MY  
SUPERVISION BY Della Darle Junkin  
ENTITLED The Separation and Identification of Acids  
in Low Temperature Tar.

BE ACCEPTED AS FULFILLING THIS PART OF THE REQUIREMENTS FOR  
THE DEGREE OF Master of Science

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## TABLE OF CONTENTS

Acknowledgment	Page
I. Introduction	1
Purpose of investigation	1
Historical	2
II. Experimental	
1. Fractionation of tar	5
a. Extraction and purification of acids	6
b. Fractionation of acids	7
c. Physical nature of acids	10
2. Extraction of acids without fractionation	10
a. Dehydration of acids	11
b. Effect of steam distillation	11
c. Effect of vacuum distillation	11
d. Use of solvents	11
e. Choice of fractional extraction solvent	12
f. Choice of precipitation solvent	12
g. Purification of solid acids	13
3. Tests to determine nature of acids	14
III. Summary and Conclusion	20
IV. Bibliography	21





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# THE SEPARATION AND IDENTIFICATION OF ACIDS IN LOW TEMPERATURE TARS.

## I. Introduction

The purpose of this investigation is to secure, if possible, the acids in low temperature tar in their original form or as nearly so as possible, and thereby gain some knowledge of the nature of the constituents of the tar and perhaps of the original coal. In the process of low temperature carbonization, there is some decomposition of the higher boiling constituents, but the amount of this is small in comparison to that produced by high temperatures. Because of this there should be found in tar some of the constituents of the coal not wholly decomposed among which many acids undoubtedly occur. The percentage of these acidic bodies known to be high in low temperature tar, their separation and identification may give some idea of the nature of those compounds which decompose on application of heat to give bodies having lower boiling points and some which later polymerize to give the higher boiling liquids and solids in tar.

By the low temperature carbonization<sup>(1)</sup> is meant the maintenance of such temperature that the formation of naphthalene and fuel oils is not begun, as a result of the decomposition of the higher boiling substances.

This transition temperature<sup>(2)</sup> occurs between 530 degrees and 560 degrees but by careful distillation a very slight decomposition can be made to occur which increases



with rapid rise in temperature resulting in a thickening which Schneider<sup>(3)</sup> attributed to be due to polymerization, and thus was he able to conclude from his work that the high boiling substances passed off undecomposed<sup>(4)</sup> from the coal in the coking process.

Professor Parr<sup>(5)</sup> says that this secondary decomposition must be prevented, and may be, by maintaining a temperature of less than 750 degrees, otherwise the "oxygenated constituents of the coal" will react with the phenol soluble substances which form the binder for the coke.

Already there have been found<sup>(6)</sup> over three hundred substances in tar, of which about one hundred fifty have been estimated and over ninety separated and purified. Among these are neutral basic, and acidic classes, containing oxygen, nitrogen, or sulphur, either in the ring or in the side chain and comprising five and six membered rings exemplified by benzene, phenol, pyridine, thiophen, and coumarone. Of all compounds contained, tar yields but few in large quantities, such as benzene, phenol, and naphthalene.

The higher homologues of phenol<sup>(7)</sup> occur in large quantities in low temperature tar both as polyhydric phenol and their esters which form resins. The latter remaining undistilled if a fractionation is made at 240 degrees and form a perfect material for road making.

Various methods have been employed for the purification of the constituents<sup>(8)</sup> of tar among which are the formation of salts of organic and inorganic reagents, with their sub-





sequent decomposition, and the use of organic solvents.

Maclaurin<sup>(9)</sup> removes bases by  $H_2SO_4$ , acids by NaOH, and the resins by means of hydrocarbon oils.

In the ordinary method of separation of tar acids, an aqueous solution of sodium hydroxide is employed, resulting in a water soluble salt of the acid which may be liberated on addition of sulphuric acid. If the specific gravity of the alkaline solution be increased, in each successive extraction, afractional separation results, with phenol and the lower boiling homologues appearing in the first extract. <sup>(10)</sup>

The percent of acids in low temperature tar is high, (fifty percent a maximum) but shows a great variation with different tars, <sup>(11)</sup> because different coals produce different types of tars; the younger the coal, the greater the yield of acids, in any given tar. <sup>(12)</sup>

When however, the acids are removed from low temperature tar there remain behind hydrocarbons which are not characteristic of any definite tar, in decided contrast to tars produced at high temperatures. These residues <sup>(13)</sup> resemble more closely petroleum products.

Heating of <sup>(14)</sup> these petroleums like paraffin hydrocarbons causes decomposition followed by polymerization to substances of aromatic nature.

Identification of phenol and its homologues has consisted of color reactions <sup>(15)</sup> and the formation of derivatives <sup>(16)</sup>. Not the least among these derivatives is the condensation with formaldehyde or with hexamethylene tetramine giving





Baekelite<sup>(17)</sup> or Redmanol<sup>(18)</sup>. Dr. Baekeland defines a "phenolic body" as one having a benzene nucleus with the hydroxyl attached to the ring either in a free or substituted form. Moreover, anhydrides<sup>(19)</sup> of the side chain hydroxyls will, if produced by very careful heating, condense to give an infusible product with formaldehyde but, if no such anhydride be present, there must be a substance of phenolic nature.<sup>(20)</sup>

Sage<sup>(21)</sup> has observed that an aqueous solution of NaOH does not remove all of the acidic substances from tar and that there remains behind dissolved in the sodium phenolate and higher homologues a large percent of the acids.

These insoluble compounds are of asphaltic type and Schneider<sup>(22)</sup> has reduced the percent of these compounds by heat and pressure to one half their original amount and secured a corresponding increase of low boiling phenols.

Marcusson<sup>(23)</sup> found that by blowing air through heated tar there were produced substances which were asphaltic in nature.

To these substances does Hubbard<sup>(24)</sup> attribute the superiority of low temperature tar to the process of road building. In the determination of the percent of "soluble bitumen" he suggests the use of carbon disulphide<sup>(25)</sup> and subsequent precipitation in hydrocarbon oil.

Robertson<sup>(26)</sup> finds pyridine a suitable solvent for the extraction of resinic and cellulosic bodies from low temperature tar.



Method and Manipulation

The method of securing the acids as nearly like those in the crude tars as possible was two fold (a) distilling the tar and extracting the acids and their subsequent fractionation and (b) fractional extraction by means of organic solvents and precipitation reagents.

The tar was dried and distilled according to the method suggested by Church.(27) There was a very large amount of foaming due to the high pyridine content and decreased but little until the last traces of water had passed over. At a temperature of 300 degrees heavy decomposition occurred and the residue in the still began to increase in volume and viscosity, finally resulting in a coke that was porous but hard and having a volume of twice that of the residue in the still at the beginning of heaviest decomposition.

TABLE I.

Crude Tar Fractionation

% H <sub>2</sub> O	.81	.72
% to 170	13.2	120
% to 230	25.9	26.9
% to 320	7.6	8.1
% to 360	8.4	9.2
% pitch	27.6	25.4
% decomposition	15.49	17.68



Each fraction as above made was treated with an aqueous solution of sodium hydroxide and the hydrocarbon removed from the alkaline solution by means of steam distillation. The acids were then liberated by the addition of sulphuric acid and a second steam distillation gave a very pure acid.

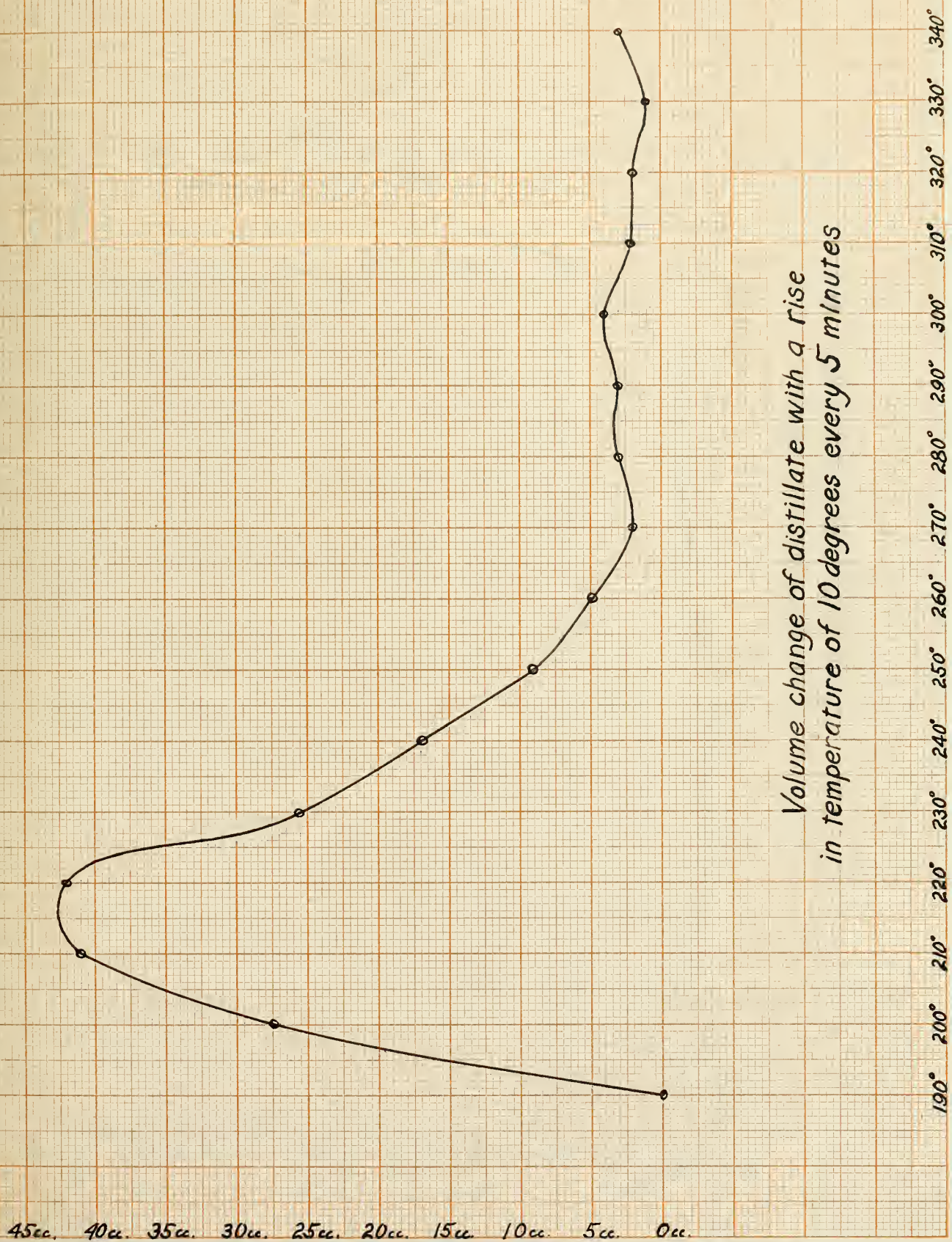
This method was successful for all low boiling phenols, but, with increase in boiling points the amount of steam needed to distill a given volume of acid rapidly increased. Moreover, there remained in the still at the end of purification of the 270 degree fraction a black viscous mass which could not be distilled with steam.

The futility of this method in securing the high boiling acids was avoided in the highest fraction by heating the alkaline solution in an open vessel thus removing any hydrocarbon and then neutralizing by the use of  $H_2SO_4$ . The resulting phenols were darker in color and more viscous than those secured by the previous method.

A sample of the acids thus purified was subjected to a time temperature distillation with a view of determining points for fractionation. The results of this process, however, showed no marked points of increase in volume for any set temperature and the amount of distillate steadily decreased with a rise in temperature. The distillate at first was water-white but on standing assumed honey yellow color. The succeeding distillates increased in depth of color and viscosity and difficulty was encountered toward the end of



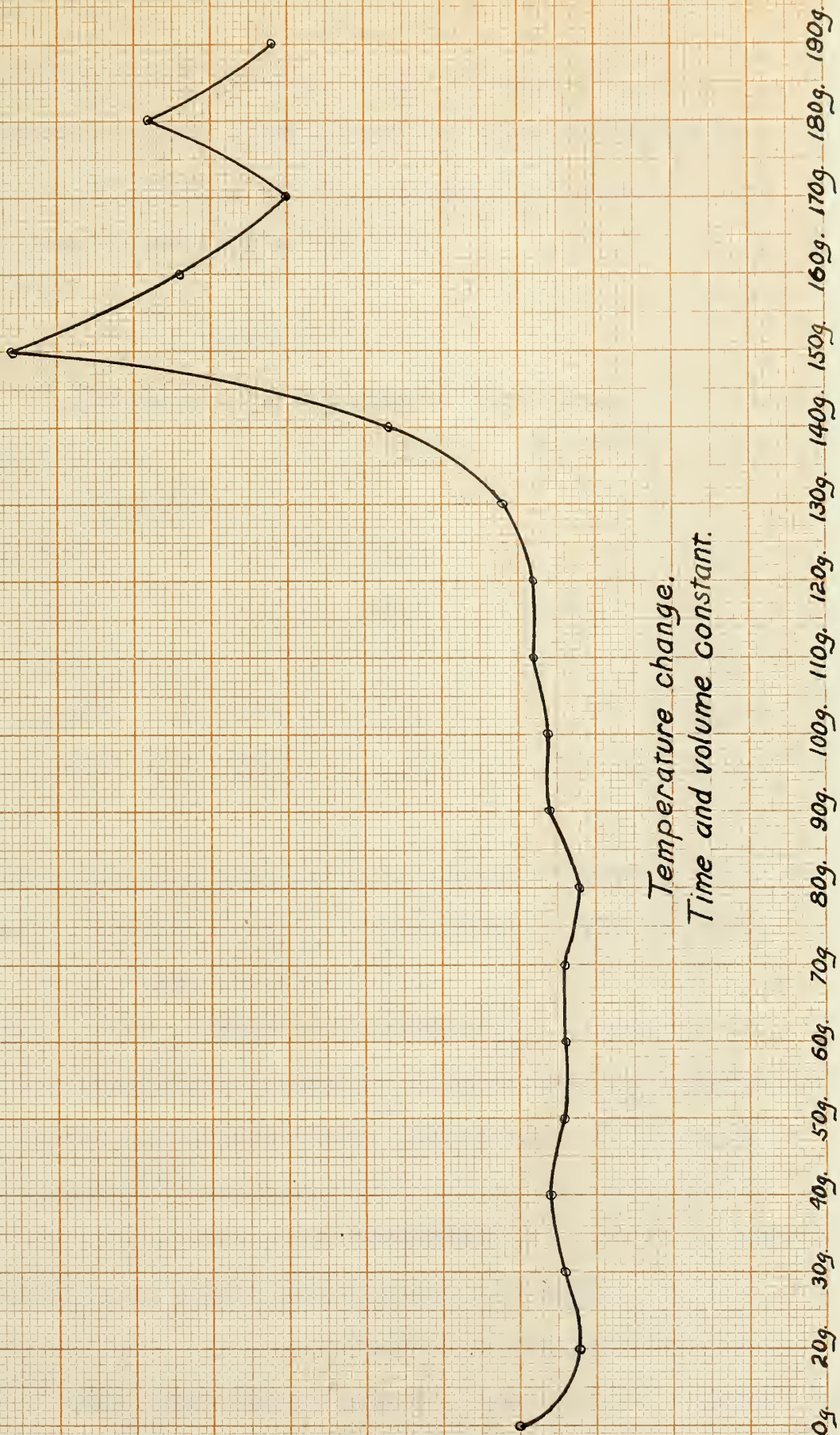








45° 40° 35° 30° 25° 20° 15° 10° 5° 0°



Temperature change.  
Time and volume constant.

10g 20g 30g 40g 50g 60g 70g 80g 90g 100g 110g 120g 130g 140g 150g 160g 170g 180g 190g



the process in the choking, of the condenser.

Another sample of the purified acids subjected to repeated distillation and the physical nature and yields noted with the following results:

TABLE II

Repeated Distillation of Pure Acids

Distillation No.	1	2	3
Vol. of Distillate			
to 170	0	0	0
230	45.6	46.3	60.3
270	23.1	18.5	11.7
320	8.1	7.7	7.4
340	4.6	4.4	2.2

From the foregoing data the amount of decomposition in the higher boiling fractions gradually increases giving bodies having lower boiling point.

The higher boiling constituents grew darker in color with each successive distillation and became so viscous as to be poured with difficulty after several such heatings.

W. Glud<sup>(28)</sup> has shown that if the high boiling tar acids are heated, their decomposition results in an increase in the yield of phenol which probable explains why the percentage of phenol is so much lower in the tar produced by the low temperature coking process than that of ordinary tars.

Fischer<sup>(29)</sup> also maintains that the percent of phenols





can be doubled by cracking tars at high temperatures.

Having found no satisfactory temperature for taking fractions, the cuts were made at those temperatures known to be about the boiling points of several substances previously found intars, ie, phenol 186 degrees, cresols 200 degrees, xylenols 210 degrees and 225 degrees.

Color tests with  $\text{FeCl}_3$  were made on these members and positive results were secured but in no case was an individual member isolated.

Comparative tests of the members of the liquid acids were made with those of the solid acids secured by the second method of extraction. This consisted in treating the crude tar with a 50% solution of potassium hydroxide. Successive extractions with the alkali finally gave an aqueous extract that contained but a small part of the acids, but still was not colored on further admixture with the tar. It was observed at the same time that all of the alkali being used was not recovered from the tar and upon examination it was found held in a black viscous emulsion below the remaining hydrocarbon layer.

Because of the extreme viscosity of this product, removal of hydrocarbon by use of a separatory funnel was impossible. To remove hydrocarbon, suction was applied and from the remaining alkaline solution the acids were liberated by means of sulphuric acid. Having washed out any potassium sulphate remaining, the acids were subjected to a combination of steam and vacuum for drying. Drying by the usual process was avoided because the viscosity of acids caused local superheating and



resulting decomposition. To avoid this the acids were warmed on a steam bath and transferred to a three liter flask having a long neck. Dry steam was passed into the warm acids and at the same time a vacuum of 600 mm. was maintained. After about 300 cc. of distillate had been collected the steam supply was shut off and the vacuum simultaneously increased to 200 mm. By this method complete dehydration was accomplished in a short time. The small amount of acids appearing in the distillate were low boiling. The yield of acids thus obtained was 36%.

A sample of the dried acid was subjected to steam vacuum distillation as applied to the drying process with the same results, ie, any acid appearing in the distillate was of the lowest boiling fraction and a yield of a few cc. per liter of steam. This low yield of acids which were transferred in the steam showed that the percent of phenol in this sample of tar was very low.

#### Extraction With Solvents.

If the acids in the tar are to be separated and examined as they are in their original form, these methods are useless. By the time a sufficiently large yield could be obtained for satisfactory observation, the nature would be so changed that their resemblance to high temperature tar acids would be closer.

Ligroin and petroleum ether were tested out as precipitating agents. Petroleum ether is more satisfactory, there being a heavy loss of all the low melting solids in the





ligroin, whereas, it was from the cold petroleum ether solution that these could be obtained and resulted in giving the nearest pure of any of the extracted products. Moreover, the high boiling point of the ligroin made sufficiently rapid evaporation by vacuum an impossibility. In no case, could there be produced a coat of ice on the outside of the filter flask and this was essential to securing the last traces of the dissolved solid acids.

The solvents tested for their extracting ability are the following, given in the order of their decreasing power to dissolve the acids: phenol, sodium phenolate, alcoholic KOH,  $\text{CS}_2$ ,  $\text{CHCl}_3$ , ether, benzene, ligroin, alcohol, and petroleum ether, of which the fractional extraction solvents chosen were phenol, carbon disulphide, chloroform, and ether.

A sample of the crude acids was extracted with ether and any undissolved residue was filtered and later treated successively with  $\text{CHCl}_3$ ,  $\text{CS}_2$ , and phenol until none remained. The ether solution was poured slowly and with constant stirring into about ten times its volume of petroleum ether and a finely divided light brown precipitate formed which filtered readily into a suction flask containing more petroleum ether previously cooled by rapid evaporation. In the filter flask another precipitate appeared and this being filtered and the filtrate as above gave second precipitate. This process was followed until no more precipitate could be secured even by using a large excess of petroleum ether at zero degrees, giving in each trial a precipitate lighter in color and more readily



soluble in petroleum ether on warming.

The chloroform, carbon disulphide, and phenol extracts were likewise treated with petroleum ether as previously, the resulting precipitation in each case darker than the preceding and much less soluble in the petroleum ether.

#### Difficulties in Extraction and Precipitation.

Carbon disulphide is a better solvent than ether, but for the separation of those acids which are soluble in petroleum ether at room temperature and precipitate on cooling,  $\text{CS}_2$  is a failure. It can not be as readily evaporated as ether by vacuum and holds all of the more soluble bodies in solution.

If the  $\text{CS}_2$  extracted be poured rapidly into the petroleum ether, the very rapid precipitation of the solute occluded liquid acids resulting in a tarry mass. This difficulty is greatly lessened if the petroleum ether is stirred rapidly and the  $\text{CS}_2$  solution added slowly. This trouble is not encountered in the case of the ether extract because the substances dissolved by ether are more readily soluble in petroleum ether.

If a filter paper is used for two or more filtrations there appears a resinous mass on the paper which causes very slow filtration. This is caused by the high boiling acids clogging the filter and then dissolving any solids to be filtered.

A purification of the precipitated acids was made in the same manner as that previously done in the extraction and



this resulted in the removal of all viscous liquid acids and a very readily filtration.

The residue that was soluble in phenol only, presented difficulties due to the fact that when the phenol solution was poured into the petroleum ether it formed a viscous mass adhering firmly to the walls of the beaker and giving no precipitate in the petroleum ether. When a small amount of ethyl ether is added to the solution, it reduces the solvent action of the phenol, and then a fine black precipitate is liberated which is readily filtered.

#### Appearance of the Purified Products.

A gradual darkening in color occurs with the rise in melting point and decreases in solubility of the solid acids separated by means of organic solvents. But one slight variation occurred in this generalization: those solid acids insoluble in the cold petroleum ether solution and having a melting point between 80-85 degrees were more distinctly orange in color than either the preceeding or following members. This characteristic became even more pronounced on repurification.

The lowest melting point of any solid obtained was 60 degrees and each succeeding sample gave a rise of from three to five degrees until that of six members was taken. It was in these latter samples that the presence of mixtures could be observed, by the transition temperature occurring





on application of heat. This became more pronounced on using those samples most easily precipitated in petroleum ether. The darker colored samples showed several transition points but no definite melting point. The phenol soluble extract had a melting point of 111 degrees and was the highest obtained.

In every case there occurred a decided change at the melting temperature. The lightest colored products became dark and viscous did not return to their former color or powdered condition on cooling. At a few degrees above the melting point decomposition set in and the product began to increase in size.

After the filtration of the acids the petroleum ether was allowed to evaporate and the resulting precipitate was powdered. All of the lower melting solids were powdered with considerable ease and had a tendency to adhere strongly to the spatula giving an easily compressed cake. Those having higher melting points possessed this property to a small extent there being a considerable decrease with increase of melting point and increase in hardness. The phenol soluble product was very compact and was reduced to a powder only after considerable pressure had been applied.





### Tests on Extracted Solid and Liquid Acids.

Numerous tests were applied to the extracted acids to determine their chemical nature, among which were solubilities, ignition, combustion, nitrogen and sulphur determination, and condensation with hexamethylene tetramine.

The solvents used were alcohol, turpentine, benzene, ether, chloroform, carbon disulphide, phenol alcoholic KOH, and pyridine.

All light colored acids precipitated by the cold petroleum ether were soluble to a greater or less extent in all solvents. Turpentine and alcohol showed the poorest solvent power.

The light brown products were soluble in all reagents with the exception of turpentine and alcohol.

The dark products showed a decided decrease in solubility in all solvents. The last extract was soluble in phenol and alcoholic KOH only.

The pyridine test was made that the asphaltic character of the products might be observed. Samples were dissolved in pyridine and some water added. On being agitated a soapy foam was produced and this remained for sometime. The addition of  $H_2SO_4$  caused the precipitation of the solute.

The solubility tests in general show that all of the substances are decidedly acidic in character, and that those lightest in color are more readily soluble in all reagents, and also that an increase in depth of color is accompanied by



a decrease in solubility.

The ignition of the liquid acids showed no characteristics other than that they were of the aromatic type. On burning all of the solid acids, however, there was a decided change. Shortly after melting they began to increase decidedly in volume and charred. This volume assumed remained constant until most of the carbon had been burned off.

To obtain the percentage composition, the determinations of carbon hydrogen and oxygen were made in a combustion furnace, nitrogen was determined by the Kjeldahl method, and sulphur as by the  $\text{Na}_2\text{O}_2$  and  $\text{KClO}_3$  fraction ation using a Parr explosion bomb. (30)

The following gives the results obtained using samples of the lightest and darkest acids:

TABLE III

Color of Samples	C	H	O	N	S
Dark ( $\text{CS}_2$ ext. )	78.6	4.3	13.6	1.5	1.11
Light (ether ext.)	78.9	5.4	13.5	1.02	1.04

From the data thus obtained there was no indication that these acids were of very great difference in molecular structure. Due to the fact, however, that these are decided mixtures an accurate determination is impossible.

To determine the position of the hydroxyl group in the molecule, ie, to ascertain if these are either carboxylic



acids or alcohols, or of true phenolic nature, Redmanol condensations were made using hexamethylene tetramine in alcoholic KOH solution, with the following results:

TABLE IV

Sample	B.P.	M.P.	Result	Residue
liquid	200-10		light brown resin	none
liquid	210-20		light brown resin	none
liquid	220-30		brown resin	none
liquid	230-60		dark brown resin	none
liquid	260-300		dark brown resin	none
liquid	300-340		black resin	light yellow ppt. in water
solid		65-85	none	original
solid		94-96	none	original
solid		104	none	original
crude tar acids			black resin	asphaltic powder.

The foregoing table shows that there are two types of acidic substances isolated by the two methods used. Those separated by distillation are of phenolic type, and may contain a small amount of the lower melting solid acids which precipitate out on condensation of the liquid acids and those bearing decided acidic properties but not of phenolic type.

The residue left from the crude tar acids after conden-





sation was the same in color and character as that obtained by the extraction methods. In this way hexamethylene tetramine may be considered as a satisfactory reagent for extraction of the higher acids.

#### Tests on Gilsonite.

Comparative tests on some asphaltene extracted from gilsonite were made, with a view to determine similarity to the solid acids obtained by extraction with one exception that there were no low melting products secured, every test applied was identical in its outcome to those applied to the acids, leading to the conclusion that these solid acids are in reality asphaltenes. (No combustion on asphaltenes from gilsonite was made).



## SUMMARY OF INVESTIGATION

1. Low temperature tar cannot be fractionated without a large amount of decomposition of the higher boiling constituents giving a porous coke having a large volume.

2. Subsequent fractionation of the tar acids causes a decrease in yields of the higher boiling constituents with a corresponding increase of the low boiling fractions.

3. No satisfactory cutting temperatures can be selected for low temperature tar acids, as there is no decided increase in yield at any one temperature.

4. Tar acids may be classed as to liquid and solids: those soluble in common organic reagents and those insoluble in all save phenol and alkali; those possessing the hydroxyl connected to the ring (truly phenolic), and those of carboxylic or alcoholic natures; and those truly acidic and asphaltic.

5. Free carbon determination in low temperature tar cannot be made as in high temperature because there is found in low temperature tar an acidic substance insoluble in benzene and  $\text{CS}_2$ .

6. The asphaltic bodies in low temperature tar decompose on heating giving an increase in the volume.



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